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13. ABSTRACT (Maximum 200 words) Two-photon absorption spectra have been measured for bis-donor diphenylpolyene derivatives with varying conjugation lengths and end groups. Large two-photon absorptivities are observed via nanosecond nonlinear transmission measurements in comparison to picosecond nonlinear transmission and two-photon excited fluorescence methods, which suggests a large contribution of excited-state absorption to the nanosecond nonlinear transmission results. Chromophores with conformationally locked bridges have been synthesized and the optical nonlinearity and thermal stability has been examined. It was found that relative to the normal polyene bridges, chromophores with confirmationally locked bridges exhibit improved thermal stability without a significant change in optical nonlinearity. A series of chromophores containing diarylamino donors have been synthesized and exhibit large optical nonlinearities, good thermal stabilities and enhance photochemical stabilities relative to compounds with dialkylamino donors. Functionalized versions of these chromophores have been synthesized for covalent incorporation into high performance polymers, for electro-optic applications.			
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**FINAL TECHNICAL REPORT FOR:**  
**CHROMOPHORES FOR ELECTRO-OPTICS AND OPTICAL SWITCHING**

Seth R. Marder

The Beckman Institute,  
California Institute of Technology,  
Pasadena, CA 91125

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## **2. OBJECTIVES**

The objectives of this work are to: 1) develop materials for protection of eyes and sensors from intense laser pulses and 2) develop novel chromophores for second-order nonlinear optical applications that exhibit large nonlinearities and other key attributes including thermal stability and solubility.

## **3. STATUS OF EFFORT**

Two-photon absorption spectra have been measured for bis-donor diphenylpolyene derivatives with varying conjugation lengths and end groups. Large two-photon absorptivities are observed via nanosecond nonlinear transmission measurements in comparison to picosecond nonlinear transmission and two-photon excited fluorescence methods, which suggests a large contribution of excited-state absorption to the nanosecond nonlinear transmission results.

Chromophores with conformationally locked bridges have been synthesized and the optical nonlinearity and thermal stability has been examined. It was found that relative to the normal polyene bridges, chromophores with confirmationally locked bridges exhibit improved thermal stability without a significant change in optical nonlinearity.

A series of chromophores containing diarylamino donors have been synthesized and exhibit large optical nonlinearities, good thermal stabilities and enhance photochemical stabilities relative to compounds with dialkylamino donors. Functionalized versions of these chromophores have been synthesized for covalent incorporation into high performance polymers, for electro-optic applications.

## 4. ACCOMPLISHMENTS AND NEW FINDINGS

### 4.1 Optical Limiters

Organic materials possessing large two-photon absorptivities can be used in optical limiters, or for intensity stabilization or pulse shaping in laser sources and devices.<sup>1-4</sup> Two-photon absorbers offer the advantage for optical limiting over reverse saturable absorbers of having a very high transmittance in the low intensity regime. On the other hand, until recently<sup>5,6</sup> the magnitudes of two-photon absorption cross sections known for organic chromophores have been too small for use in optical limiting of nanosecond (ns) laser pulses. We have recently shown that bis(*di-n*-butylamino)stilbene (**1** in Figure 1) exhibits a large two-photon absorptivity at 600 nm measured by two-photon fluorescence, as shown in Table 1. In addition a very large *effective* two-photon absorption cross section,  $\delta$ , of about  $1.7 \times 10^{-46}$  cm<sup>4</sup> s/photon-molecule was obtained by way of a nonlinear transmission (NLT) experiment using ns pulses.<sup>5</sup> However, a strong dependence of this effective nonlinearity on pulse duration was observed<sup>4</sup> and this result has raised questions regarding the origin of the large apparent two-photon response on the ns timescale for **1** and related molecules.

In this this section, we report on: 1) the dispersion of the nonlinear absorption for a series of bis-donor substituted diphenyl-polyenes and the correlation of molecular structure (conjugation length and alkylamino *versus* arylamino end groups) with the nonlinear absorption dispersion; 2) a comparison of results obtained using the nonlinear transmission method with ns and ps laser pulses, and the two-photon excited fluorescence method; and 3) a demonstration of broadband optical limiting over a wide wavelength range in the visible based on a tandem cell arrangement involving three different bis-donor compounds.

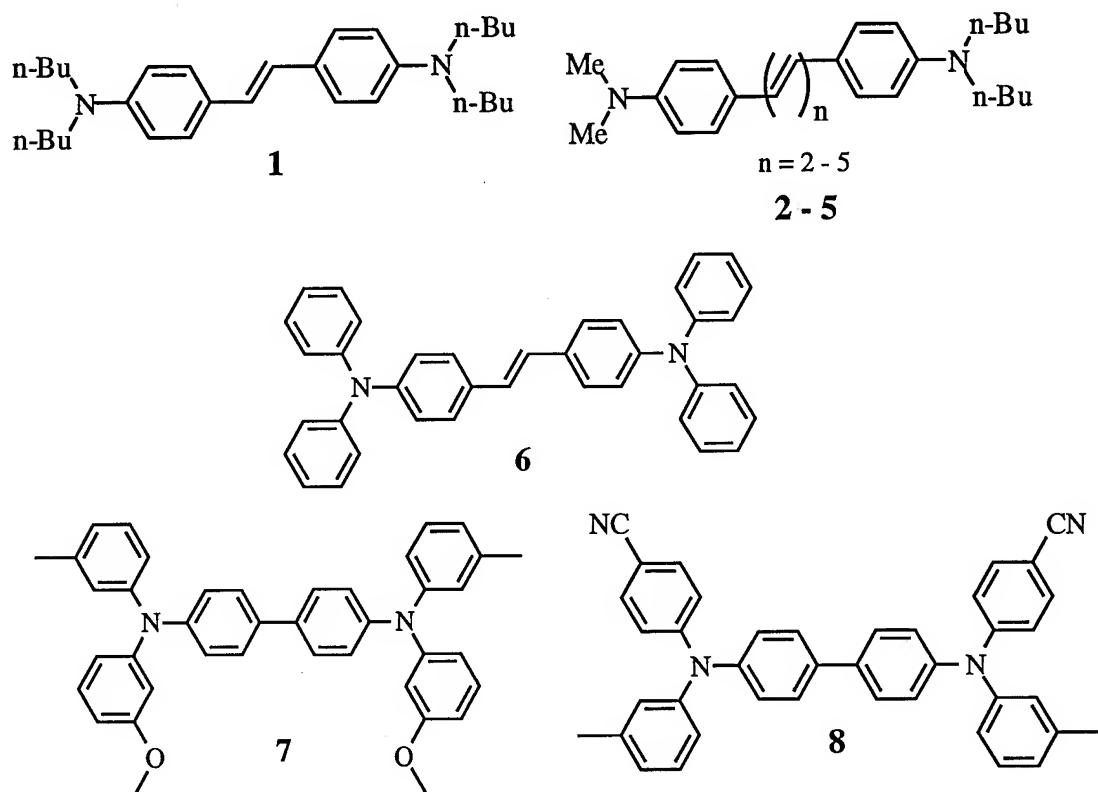


FIGURE 1 Structures of the compounds studied in this work.

Comparison of nonlinear absorption dispersion by nonlinear transmission and two-photon excited fluorescence methods.

Figure 1 shows the molecular structure of the compounds studied in this work. Nonlinear optical measurements were performed as described in reference 7. We have previously reported that compound **1** exhibits,  $\delta_{\text{eff}}$  values (by nanosecond nonlinear transmission (NLT) methods) of  $1.6 \times 10^{-46}$  in acetone and  $7.5 \times 10^{-47} \text{ cm}^4 \text{ s/photon-molecule}$  in toluene at 605 nm. The  $\delta_{\text{eff}}$  values for **2** are  $6.3 \times 10^{-47}$  in acetone and  $2.1 \times 10^{-47} \text{ cm}^4 \text{ s/photon-molecule}$  in toluene. The nonlinear transmission measurements have been extended for compounds **1** and **2-5** to cover the wavelength range from 550 to 850 nm<sup>7</sup>. Figure 2 shows the effective two-photon absorption spectra obtained for compounds **1**, **2** and **4**.<sup>4</sup> In comparison, Figures 3a and 3b, show the spectra of **1** and **2-5** as obtained from two-photon excited fluorescence (TPF) measurements. It is evident from the comparison of Figure 2 and Figures 3a and 3b, that the

values of the absorptivity derived from the two different methods differ by more than an order of magnitude, but that the position of the peak and the overall shape of the spectra are very similar.

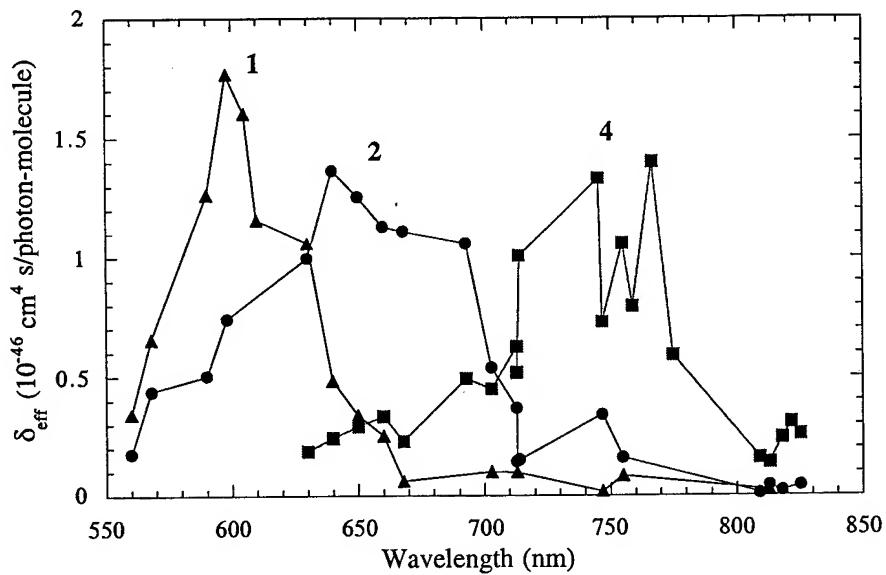
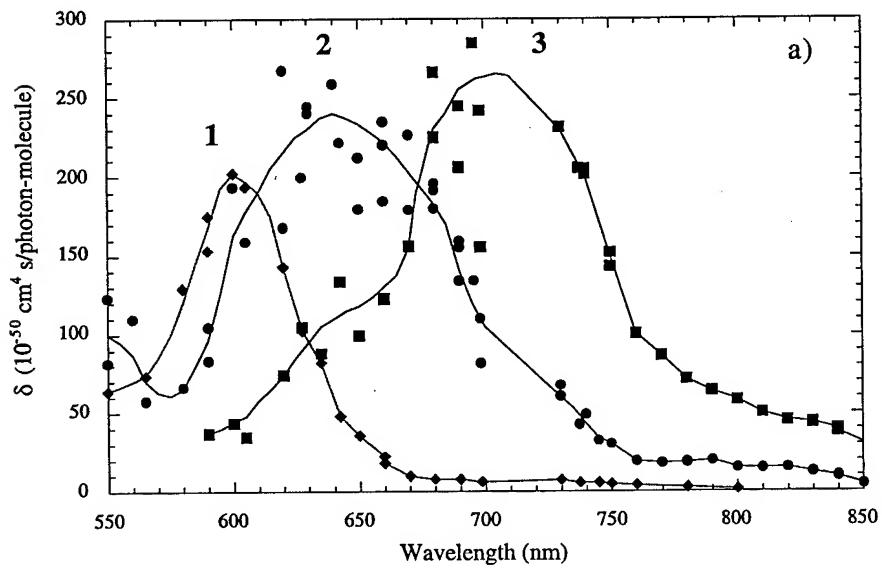


FIGURE 2 Dispersion of the effective two-photon absorptivity for **1** in acetone ( $\blacktriangle$ ), **11** in toluene ( $\bullet$ ) and **13** in toluene ( $\blacksquare$ ), as measured by nonlinear transmission using 5-ns laser pulses. The connecting lines are provided as a guide to the eye.



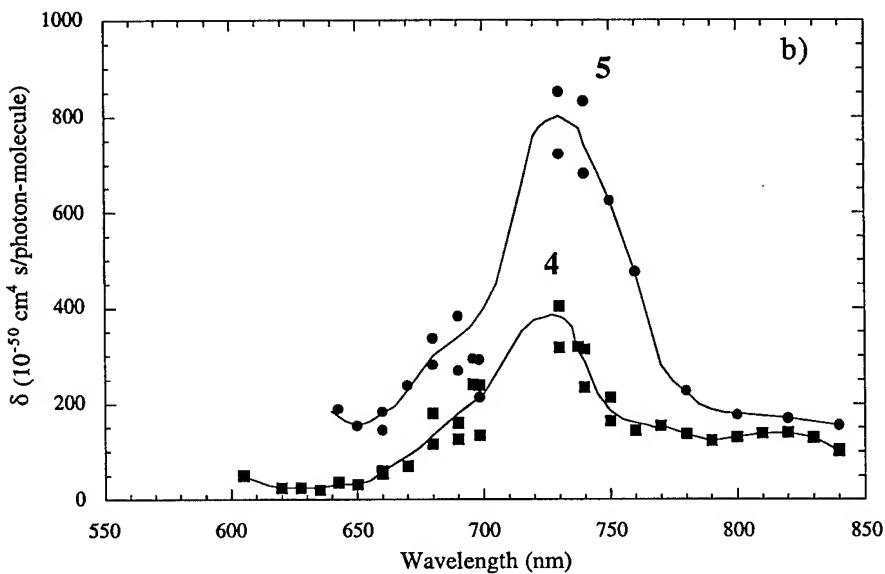


FIGURE 3 Two-photon absorption spectra of a) 1 (◆), 2 (●), 3 (■) and b) 4 (■) and 5 (●) as derived from two-photon excited fluorescence measurements. All molecules were dissolved in toluene at a concentration of about  $10^{-4}$  M. The curves are provided as a guide to the eye.

The increase in the conjugation length in the series **1** and **2-5** results in a red shift of the peak position of the two-photon absorption band,  $\lambda^{(2)}_{\text{max}}$ , from 600 nm for **1** to 730 nm for **14**, as observed for the TPF data.

#### Pulse Width Dependence and Role of Excited-State Absorption

To investigate further the difference in magnitude of the observed two-photon absorptivities measured by nanosecond NLT and TPF measurements, we performed studies of the NLT response using ps laser pulses<sup>7</sup>. We found that the ps NLT results are more than an order of magnitude lower than their ns NLT counterparts, whereas they are in reasonable agreement with the results of the TPF technique.

If the mechanism responsible for the nonlinear transmission is a pure two-photon process, one would expect  $\delta$  to be pulse-width independent, providing that there is not a substantial depletion of the ground state population during the excitation. However, as population builds up in the lower excited states,  $S_2$  or  $S_1$ , as would be the case under the prolonged excitation from a ns laser pulse, absorption from these states to higher lying excited states,  $S_n$  (excited-state absorption), can take place and contribute to the overall nonlinear loss. Such a two-photon induced excited state absorption process is a doubly resonant three-photon absorption, as illustrated in Figure 4.

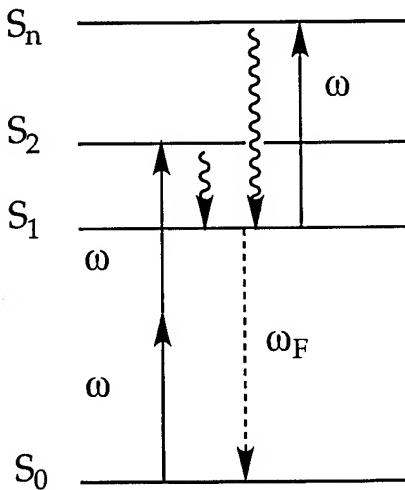


FIGURE 4 Schematic representation of the energy levels involved in two-photon absorption and two-photon induced excited-state absorption processes.  $S_0$  is the ground state,  $S_1$  is the first-excited state,  $S_2$  is the second-excited state (two-photon allowed), and  $S_n$  is a generic, higher energy, excited state.  $\omega$  is the frequency of the exciting photons,  $\omega_F$  is the frequency of the fluorescent photons.

We have modeled the ns NLT response of 1 as a combined two- and three-photon absorption process and obtained an estimate of the three-photon absorption coefficient,  $\sigma_3$ , of  $\sim 3 \times 10^{-73} \text{ cm}^6 \text{ s}^2/\text{photon}^2\text{-molecule}^7$ . The effective three-photon cross section obtained is

proportional to  $\sigma_e$ , the excited-state absorption cross section, which we have estimated to be about  $8 \times 10^{-17} \text{ cm}^2$ , for **1** in toluene. Our studies indicate that for molecules with such a large  $\sigma_e$ , and a moderately large  $\delta$ , of the order of  $10^{-48} \text{ cm}^4 \text{ s/photon-molecule}$ , the two-photon induced excited-state absorption process will make a significant contribution to the overall nonlinear loss in a ns nonlinear transmission measurement.

#### Design of Broadband Optical Limiting Materials

For optical limiting applications, very large nonlinearities over a wide bandwidth are typically needed. We previously reported<sup>5</sup> an approach to obtain relatively broadband nonlinear absorption, simultaneously with high transparency, based on bis-donor stilbenes. Replacement of the dialkylamino groups in **1** with diphenylamino groups, leading to **6**, resulted in a 90 nm red-shift in the effective two-photon absorption peak, but little loss of transparency at wavelengths  $> 450 \text{ nm}$ .<sup>5</sup> Thus a mixture of **1** and **6** gave rise to a nonlinear absorption bandwidth of  $\sim 170 \text{ nm}$  and high linear transmission. However, superposition of the nonlinear response of **1** and **6** leaves the spectral region ranging from 500 to 550 nm, where the linear transmission is very high, with negligible nonlinear absorption. In order to fill this gap, we considered the design of molecules with smaller conjugation length and bis(diarylamino) substitution. As we will show below, on going to a biphenyl bridge the two-photon absorption peak blue-shifts to  $\sim 525 \text{ nm}$ .<sup>7</sup>

We examined the magnitude and dispersion of the two-photon absorptivity for **7** and **8** using ns NLT and ns TPF measurements<sup>7</sup>. We obtained  $\delta$  values for compounds **7** and **8**, as determined by ns TPF measurements, of  $\sim 250 \times 10^{-50} \text{ cm}^4 \text{ s/photon-molecule}$ . Through our measurements of the ns-NLT response, we found there is a strong two-photon induced excited-state absorption contribution for **7** and **8**. These data were analyzed as described above resulting in  $\sigma_3$  for **7** and **8** of  $2.8 \times 10^{-73}$  and  $0.7 \times 10^{-73} \text{ cm}^6 \text{ s}^2/\text{photon}^2\text{-molecule}$ , respectively. These results show that for **7**, which possesses electron donating methoxy groups, there is a larger effective  $\gamma$  than for **8**, which has electron accepting cyano groups.

In order to assess the utility of the bis(diarylamo) biphenyl compounds for use in a broadband optical limiter, we measured<sup>7</sup> the dispersion of the two-photon absorption for **7**, which is shown in Figure 5, along with the data for **1** and **6**, reported previously.<sup>5</sup> The center wavelength of the two-photon absorption band for **7** occurs at 525 nm. The band position is in the range to partially fill the gap in the spectral range of the nonlinear absorption dispersion for **1** and **6**. Accordingly, a limiting material based on an additive combination of the response of all three molecules would provide nonlinear absorptivity over an extremely broad spectral range (~250 nm), and maintain high linear transmission, >90%, over the same range. As a simple demonstration of the broadband limiting response, we examined the optical limiting of solutions of **1**, **6** and **7** in a triple-stacked tandem cell geometry, at 600 nm and 532 nm in a collimated beam (f/23) optical system. The triple-stack tandem cell contained three compartments, each with a 1-mm optical pathlength. Our results showed that the triple-stack tandem sample performed well at the two wavelengths used in the test.

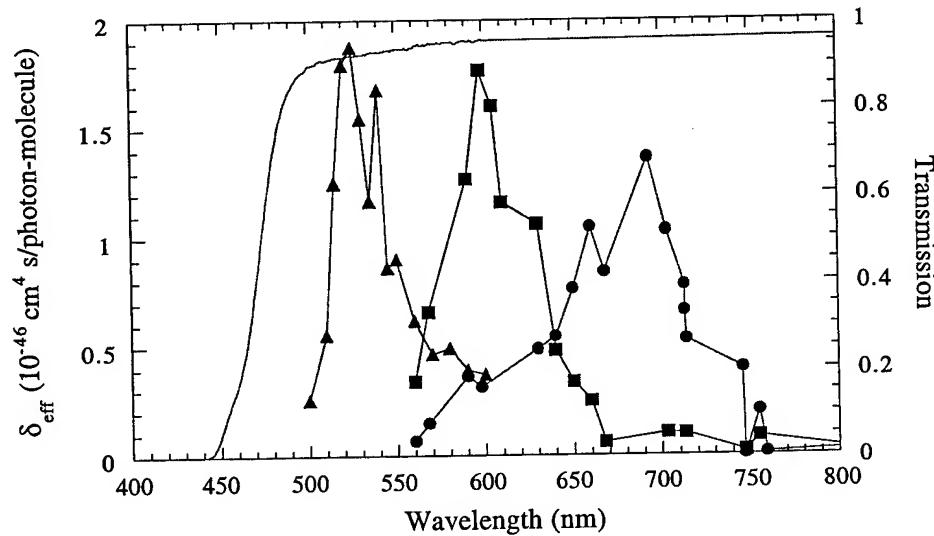


FIGURE 5 Spectrum of effective two-photon absorptivity for **1** (■), **6** (●) and **7** (▲), in toluene at 0.01 M concentration. The solid curve without points is the linear transmission spectrum for a triple-stacked arrangement of cells containing toluene solutions of **1**, **6** and **7** at 0.1 M.

In summary, our studies provide strong evidence that two-photon induced excited-state absorption can make a significant contribution to the effective nonlinearity in ns nonlinear transmission measurements. We have shown that bis-donor substituted diphenylpolyenes exhibit large effective two- and three-photon cross sections, which can be tuned by varying the length of the polyene bridge and modifying the substituents on the terminal amino groups. We have also shown that this control over the strength and position of the effective nonlinear absorption cross sections allows the design of materials for broadband optical limiting and high linear transparency. A demonstration of this strategy, that makes use of a simple triple cell tandem geometry, has been described.

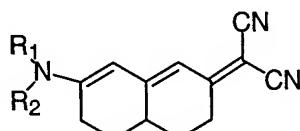
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## 4.2 Photorefractive Polymer Design

Recently, studies have shown that molecules such as A can act as NLO chromophores and also as photocharge generators but the response is slow. The goal of this work is to design and synthesize molecules that incorporate amines which lead to improved hole transporting properties to increase the speed of the response.



A. R<sub>1</sub> = R<sub>2</sub> = Hexyl

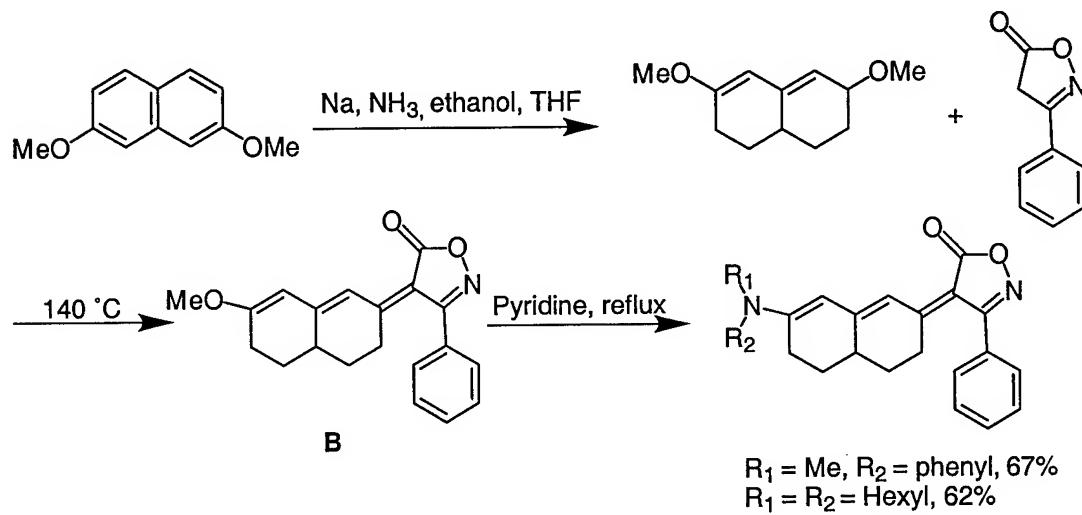
Following the previous results, we have focused our studies on the system of donor-acceptor substituted polyene chain with two double bonds which are rigidly linked by incorporation into 3,4,5,6,10-pentahydronaphthalene. On the molecular level, according to the oriented gas model. PR effect may be defined by following equation.

$$\mathbf{F} = \mathbf{A}(T) \Delta\alpha\mu^2 + \beta\mu$$

Where  $\Delta\alpha$  is the polarizability anisotropy of the chromophore,  $\mu$  is its dipole moment,  $\beta$  is its first hyperpolarizability,  $A(T) = 2/(9KT)$  is scaling factor. Linear molecules such as polyenes exhibit a considerable charge transfer that is confined along the quasi one dimensional  $\pi$ -conjugated bridge providing a large  $\Delta\alpha$ . In addition, polyenes can have an important charge separation in the ground state that provide larger  $\mu$ . The bridged pentahydronaphthalene is also enhanced thermal and photochemical stability. Triphenylamine and carbazole derivatives are known as good hole transportors. We incorporated them in to the donor parts of chromophore molecules.

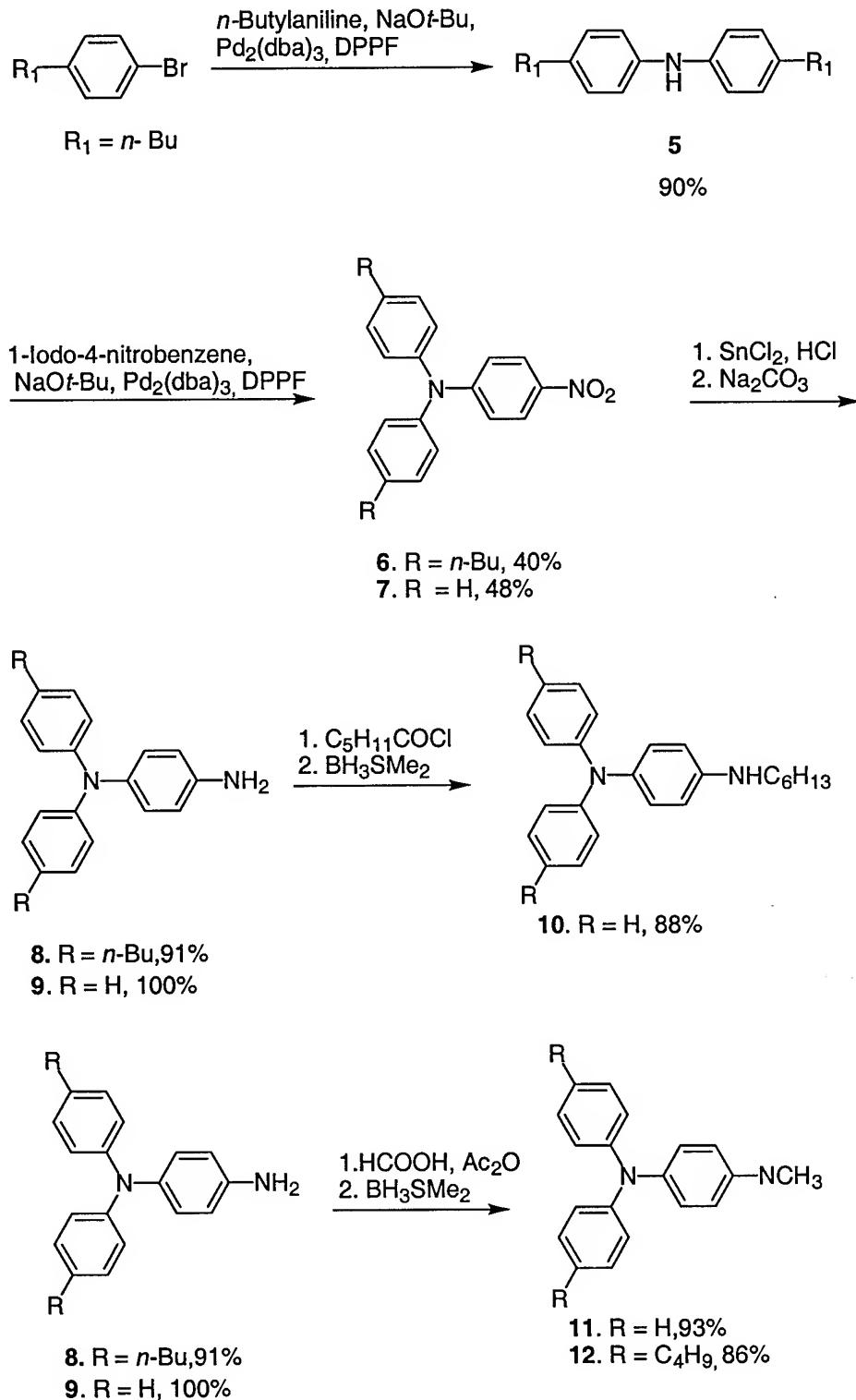
Compound B has been made before in our lab. The synthesis is shown in scheme 1. The coupling reactions between amine donors and B was tested in simple systems first with moderate yield of products.

Scheme 1



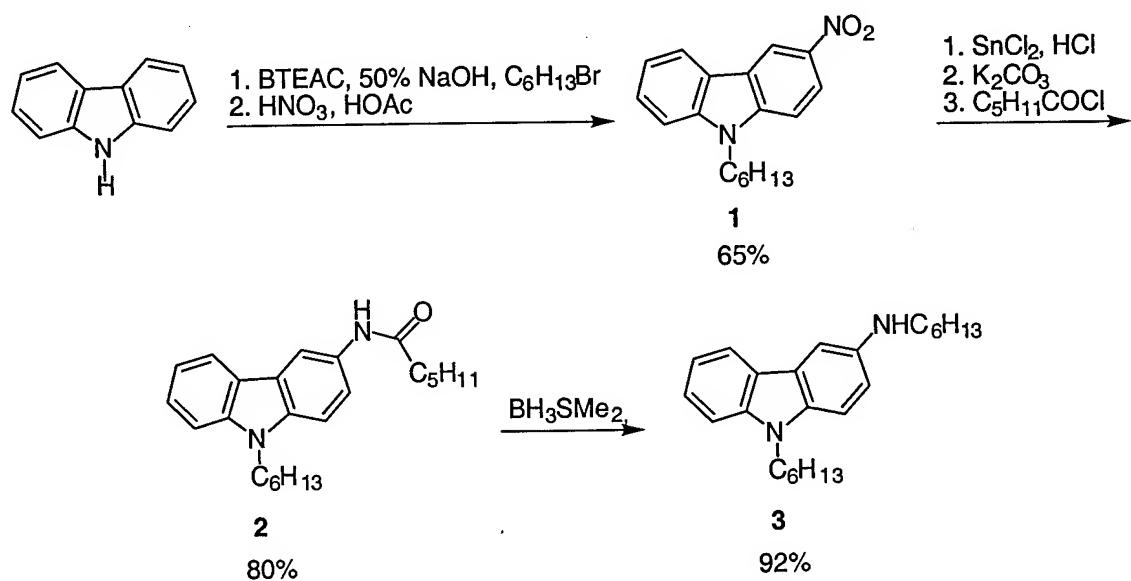
Our major effort is devoted to synthesis the donor part of molecules. Triphenyl amine derivatives were made in five step synthesis with 40% of overall yield (scheme 2).

**Scheme 2**



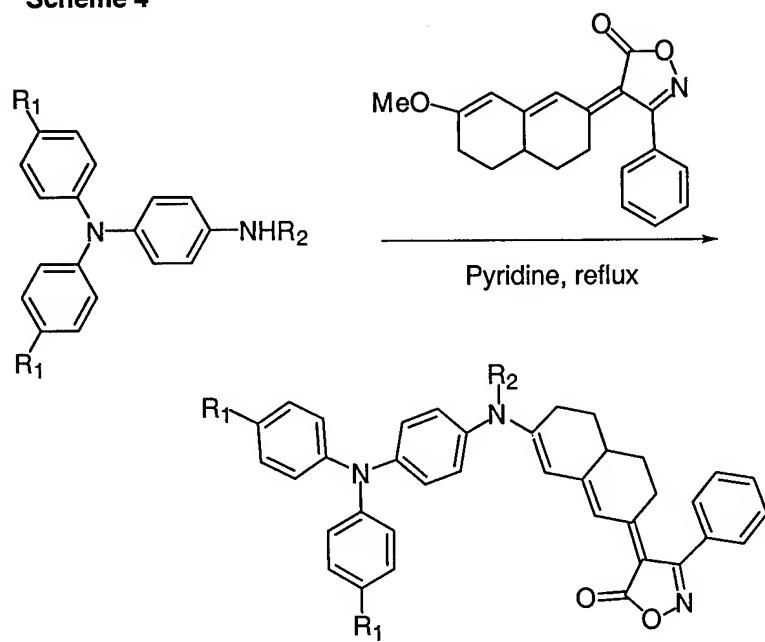
Carbazole derivatives were also synthesis in five steps with overall 48% of yield (scheme 3).

**Scheme 3**

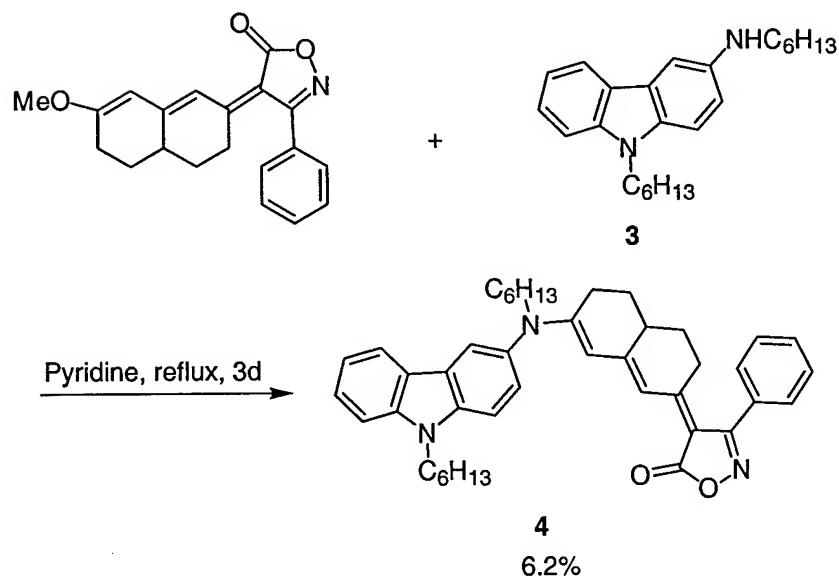


The reactivity of the triphenylamine derivatives and carbazole derivatives depends on the substitutions on the amino group. The large alkyl groups such as hexyl give lead to slow reactions and low product yields. Small groups such as methyl group were more and give better yield (Scheme 4).

**Scheme 4**



14. R<sub>1</sub> = H, R<sub>2</sub> = CH<sub>3</sub>, 52%.  
15. R<sub>1</sub> = C<sub>4</sub>H<sub>9</sub>, R<sub>2</sub> = CH<sub>3</sub>, 64%.  
18. R<sub>1</sub> = H, R<sub>2</sub> = C<sub>6</sub>H<sub>13</sub>, 2.6%



**References and notes**

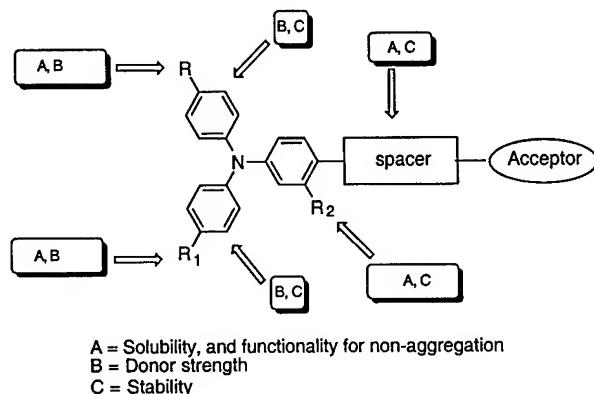
### **4.3 Design and Synthesis of Thermally and Photochemically Stable Electro-Optic Chromophores with High Optical Nonlinearity**

#### **Introduction:**

The interest in electro-optic materials has grown in the recent years due to the potential applications in optical data storage and optical information processing.<sup>12</sup> One of the promising approaches towards these materials involves poled polymers. Recently, a simple model has been put forth which correlates the hyperpolarizability  $\beta$  with the ground state polarization of the chromophore to design molecules with high optical nonlinearity.<sup>3</sup> However, in addition to high nonlinearity, the chromophores should exhibit additional features such as thermal stability, photochemical stability, minimal aggregation, and compatibility with the polymer host. Thermal stability is an essential feature, since, during device fabrication, the dipole of the chromophores are aligned by applying an electric field at temperatures above the glass transition temperature ( $T_g$ ) of polymer host. The  $T_g$ 's of the commonly used high performance polymers are over 200 °C and therefore it is imperative that the organic chromophores exhibit high thermal stabilities above 200 °C.<sup>45</sup> We also believe that the organic NLO chromophores should be photochemically stable to ensure the longevity of electro-optic devices. The electro-optic materials are exposed to high intensity light during device operation and therefore incorporation of photochemically less stable chromophores are prone to degradation with time. In addition, the chromophores also should be miscible with the polymer host to reduce chromophore aggregation.<sup>6</sup> Reduced aggregation would result in a material with homogeneous refractive index, thus diminishing optical loss due to scattering. Aggregation of chromophores is a common problem encountered in materials with high chromophore loading and in chromophores with huge dipole moments. The problem is often tackled by introducing bulky substituents around the chromophores to reduce aggregation.

Here, we report a design in which all these features are taken into consideration. The design feature of the chromophore constitutes a diarylamino donor moiety connected through a styryl thiophene conjugated bridge to an acceptor.<sup>7</sup> The aryl substitution on the donor moiety serves to enhance the thermal and photochemical stabilities of these chromophores. The substituents on the aryl groups and the substituents on the conjugated bridge serve to increase the solubility of the chromophores and also presumably provide the steric hindrance to reduce aggregation in the polymer host. The substitutions on the aryl groups are also used to tune the donor strength of the chromophores without compensating other advantageous features. We demonstrate here that the chromophores synthesized using this design exhibit enhanced thermal stabilities and optical nonlinearities. For the first time, we also report that our current design

strategy is useful in improving the photochemical stability of the second order NLO chromophores.

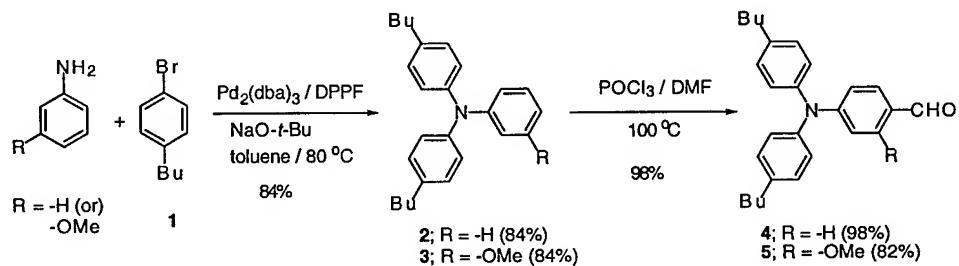


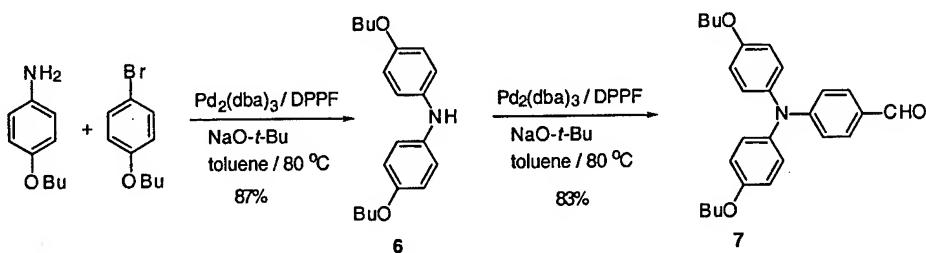
**Figure 1.** Chromophore Design Features

### Synthesis:

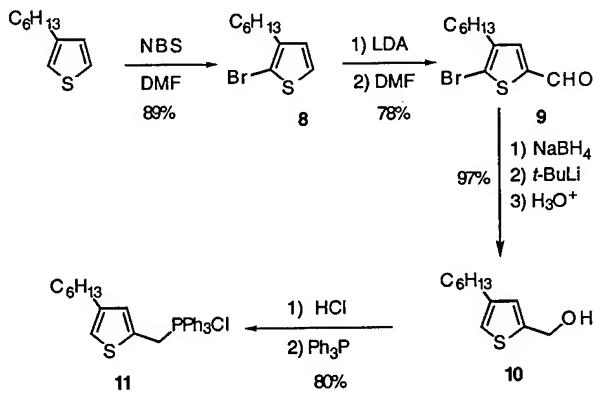
We approached the syntheses of these chromophores in a convergent fashion. The donor triarylamine was synthesized as an aldehyde and the thiophene spacer was synthesized as a phosphonium salt. The main skeleton of the chromophore was then assembled together by Wittig reaction. The acceptor group was installed in the last step of the synthesis.

The triarylamine was assembled using the palladium catalyzed aryl carbon-nitrogen bond forming reaction reported in the literature recently.<sup>89</sup> The triarylamine is then subjected to Vilsmeir-type reaction conditions to afford the (*p,p'*-dibutyl)diphenylaminoaryl-4-carboxaldehydes **4** and **5**. The synthesis of 4-(*p,p'*-dibutoxy)diphenylaminobenzaldehyde (**7**) is synthesized through two palladium catalysis steps.

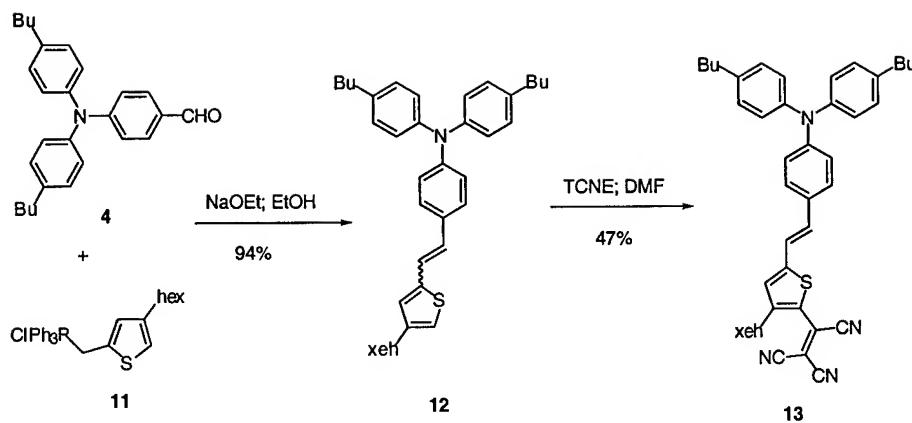




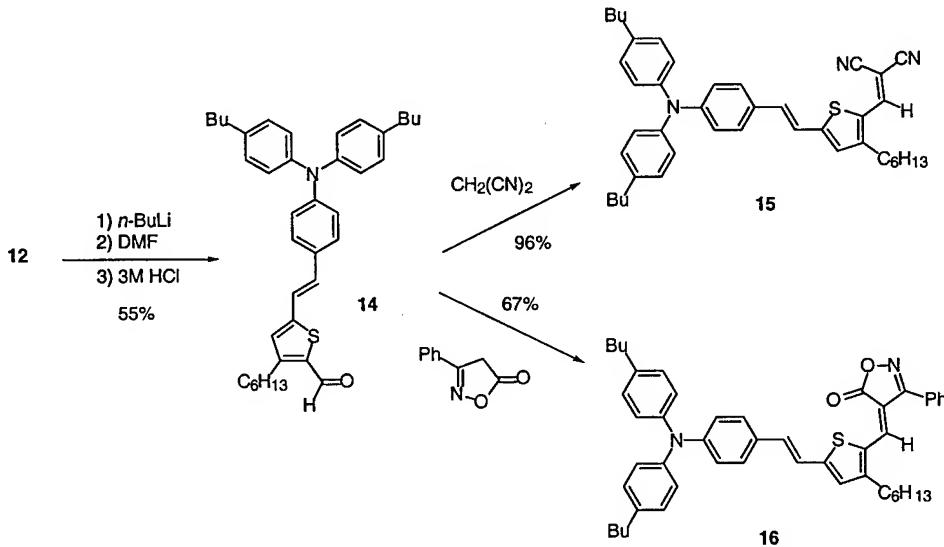
The synthesis of 4-hexylthiophene-2-methylenetriphenylphosphonium chloride (**11**) was approached with commercially available 3-hexylthiophene as the starting substrate. Bromination of 3-hexylthiophene with *N*-bromosuccinimide proceeded affords 2-bromo-3-hexylthiophene (**8**). This bromo- group is being used as the protecting group for the site-selective lithiation in the next step using LDA and DMF to afford **9** in 78% yield. Reduction of the aldehyde to the corresponding alcohol followed by deprotection of the bromo group provided the alcohol **10** in 97% overall yield. The alcohol was then converted to the phosphonium salt **11** through the choloride.



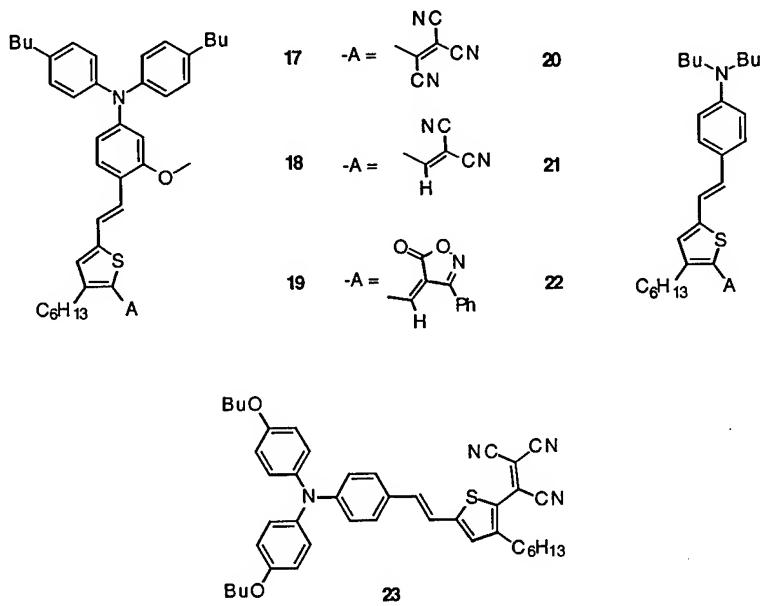
Reaction of **4** with **11** under Wittig reaction conditions using sodium ethoxide as the base afforded the product **12** as a mixture of the cis- and trans- isomers. Treatment of this mixture with tetracyanoethylene (TCNE) in DMF at 50 °C afforded the chromophore **13** with the tricyanovinyl group as the acceptor in 47% yield. The chromophore **13** had only the trans product. The tricyanovinyl group, being a strong acceptor, should have significant contribution from the charge transfer form of the structure, thus providing an opportunity for compound **13** to isomerize to the thermodynamically favorable trans isomer.



The chromophores **15** and **16** with dicyanovinyl and phenylisoxazolone as the acceptors were also synthesized. For this purpose, we synthesized the aldehyde **14** from **12** by deprotonating the thiophene and treating the resultant organolithium intermediate with DMF. The compound **14** was obtained as a 6:4 mixture of trans and cis isomers. Treatment of this mixture with 3M aqueous hydrochloric acid in THF improved the composition to a 20:1 mixture as estimated by <sup>1</sup>H NMR. Subjecting the aldehyde Knovenagel condensation with malononitrile and 3-phenylisoxazolone affords the chromophores **15** and **16** respectively.

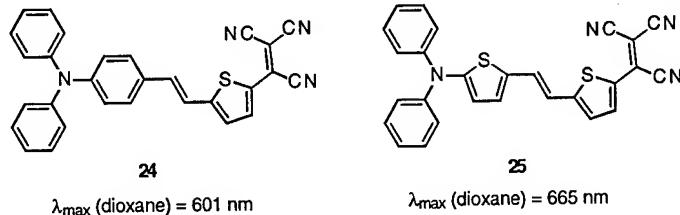


The methoxy substituted chromophores **17-19** were synthesized through the same route by using **5** in the place of **4**. Similarly the chromophores **20-22**, with dibutylamino moiety as the donor was synthesized by the same route by using the commercially available 4-(*N,N*-dibutylamino)benzaldehyde in the place of **4**. Chromophore **23** was synthesized using **7** as the precursor by adapting the same route used for the synthesis of the chromophore **13**.



### Linear Optical Spectra:

We previously reported diphenylamino substituted phenyl and thiophene stilbene compounds which had high optical nonlinearities.<sup>5a</sup> The diphenylaminothiophene based chromophore **25** had higher optical nonlinearity than the diphenylaminophenyl chromophore **24**. However, the thermal stability of **25** is inferior to that of **24**. To synthesize diphenylaminophenyl chromophores with higher optical nonlinearities, the donor strength of the chromophores were increased. Installing two butyl groups on the phenyl rings in **13** resulted in a red shift of about 23 nm from **24**. When we increased the electron density of the bridging phenyl ring by installing a methoxy group meta- to the diphenyl amino moiety, red shift of about 21 nm in CH<sub>2</sub>Cl<sub>2</sub> and 11 nm in dioxane are observed for the compound **17**. Installing two butoxy groups on the terminal ring or one methoxy group on the bridging phenyl ring have comparable effects on the linear spectra of these chromophores.



**Table I:** Linear Optical Data of the NLO Chromophores

Entry	Compound	$\lambda_{\max}$ (dioxane)	$\lambda_{\max}$ (CH <sub>2</sub> Cl <sub>2</sub> )	$\epsilon$ (CH <sub>2</sub> Cl <sub>2</sub> )
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1	<b>20</b>	645	702	36950
2	<b>13</b>	624	669	38580
3	<b>17</b>	635	690	44510
4	<b>23</b>	641	684	40230
5	<b>21</b>	535	558	42650
6	<b>15</b>	520	538	41760
7	<b>18</b>	528	551	41080
8	<b>22</b>	572	600	48990
9	<b>16</b>	552	570	41410
10	<b>19</b>	560	587	42660

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### **Electrochemistry:**

Since these NLO chromophores experience significant electric fields during poling and during the operation of the devices, it should be of interest to study the electrochemical behaviour of the compounds. All the chromophores reported in Table II have reversible oxidations independent of the donor or the acceptor group. The dependence of oxidation potential on the nature of the acceptor attests the effective communication between the donor and the acceptor. However, the reversibility of the reduction wave depends on the nature of the acceptor. It is interesting to note that the chromophores which do not display reversible reduction potentials have a vinyl hydrogen in the acceptor moiety, while the chromophores which do have reversible reduction waves lack the vinyl hydrogen in the acceptor moiety. For example, the NLO chromophores with dicyanovinyl moiety as the acceptor group **26-29**, all of which have a substitution at the  $\beta$ -position, exhibit fully reversible reduction waves.<sup>10</sup> The reason for such an

effect and the possible implications in the stability of the chromophores are currently under investigation.

**Table II:** Cyclic Voltammetry Data

	Donor	Acceptor	$E_{1/2} [m^+/m^-]$ (mV)	$E_{1/2} [m/m^-]$ (mV)
20	Bu <sub>2</sub> N-	-(CN)C=C(CN) <sub>2</sub>	321	-992
13	Ar <sub>2</sub> N-	-(CN)C=C(CN) <sub>2</sub>	408	-948
17	Ar <sub>2</sub> N-Ar'(OMe)-	-(CN)C=C(CN) <sub>2</sub>	367	-960
23	(BuO-Ar) <sub>2</sub> N-	-(CN)C=C(CN) <sub>2</sub>	264	-955
21	Bu <sub>2</sub> N-	-CH=C(CN) <sub>2</sub>	268	-1594 <sup>b</sup>
15	(Bu-Ar) <sub>2</sub> N-	-CH=C(CN) <sub>2</sub>	370	-1573 <sup>b</sup>
18	Ar <sub>2</sub> N-Ar'(OMe)-	-CH=C(CN) <sub>2</sub>	327	-1533 <sup>b</sup>
22	Bu <sub>2</sub> N-	-CH=isoX	242	-1461 <sup>b</sup>
16	(Bu-Ar) <sub>2</sub> N-	-CH=isoX	359	-1444 <sup>b</sup>
19	Ar <sub>2</sub> N-Ar'(OMe)-	-CH=isoX	314	-1353 <sup>b</sup>

<sup>a</sup>  $E_{1/2}$  relative to Fc<sup>+</sup> / Fc in CH<sub>2</sub>Cl<sub>2</sub> (0.1M (*n*-Bu<sub>4</sub>N<sup>+</sup>)(PF<sub>6</sub><sup>-</sup>)). <sup>b</sup> Maximum of the reduction peak is reported. The overall process is not reversible.

### Nonlinearity:

The EFISH measurements on these chromophores are being studied. The electro-optic coefficient was measured for the chromophores **13** incorporated into a polyimide material as a

host-guest system. Very uniform thin films (1-2 mm) of guest/host polyimide (20 wt% of **13** in pre-imidized AMOCO-Ultradel-4212) were prepared by spin-coating the polymer solution (12.5 % m/m, filtered through a 0.2 mm syringe filter) in cyclopentanone onto an indium tin oxide (ITO) glass substrate. The films were heated in a oven at 150 °C for 20 minutes to ensure the removal of residual solvents. The dipole alignment of the NLO chromophores in the polymer film were achieved by contact poling at 192 °C. Preliminary results showed that the NLO polyimide exhibited a large electro-optic coefficient ( $r_{33}$ ) value and good temporal stability of dipole moment at elevated temperature. The poled polyimide exhibited an  $r_{33}$  value of 18 pm/V measured at 1.3 mm with a poling field of 1 MV/cm. The  $r_{33}$  value remained at 12 pm/V (67 % of the original value) at 80 °C in vacuum for more than 1000 hours (Figure 1).

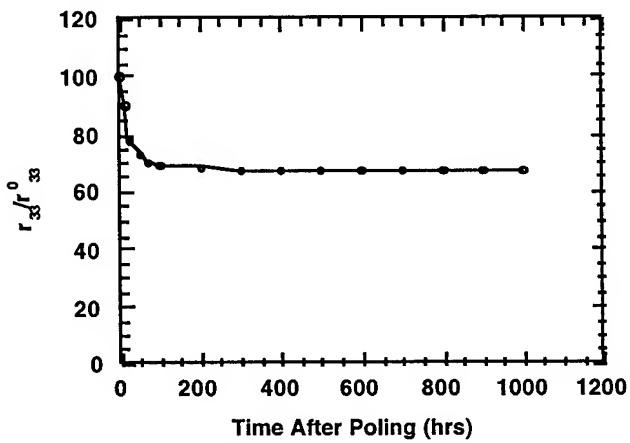


Figure 1. Temporal stability of the poled guest/host polyimide at 80°C in vacuum oven (normalized  $r_{33}$  as a function of baking time)

### Thermal Stability:

The onset of thermal decomposition of the chromophores reported here were measured by thermogravimetric analysis. The thermal stability of the chromophores depend on the nature of the donor moiety. The thermal stability of the chromophores with diarylamino groups as donor moieties have significantly increased compared to their counterparts with dialkylamino moieties (compare entries 1 vs. 2 and 5 vs. 6 in Table III). There is a remarkable difference between the dialkylamino and diarylamino chromophores **20** and **13**, while the effect is slightly less pronounced with chromophores **21** and **15**. There was essentially no thermal stability enhancement with **16** compared to **22**.

The relative thermal stabilities also clearly showed a dependence on the acceptor moiety. The chromophores with dicyanovinyl group are stable at temperatures over 300 °C (entries 5-7),

while the corresponding chromophores with tricyanovinyl moiety are relatively less stable (entries 1-4). Chromophores with phenylisoxazolone acceptor group decomposes at around 230 °C independent of other functionalities. At this temperature, there is a small, yet significant loss of weight at this temperature. In fact, when the chromophore **22** is heated at 250 °C for 20 minutes, the peak corresponding to the C=O stretching at 1743 cm<sup>-1</sup> disappeared in the IR spectrum. This is taken to indicate that the thermal decomposition at this temperature involves the phenylisoxazolone acceptor moiety.<sup>11</sup>

**Table III:** Thermal Decomposition of the NLO Chromophores

Entry	Compound	R <sub>2</sub> N-	Acceptor	T <sub>d</sub> ( °C)
1	<b>20</b>	Bu <sub>2</sub> N-	-(CN)C=C(CN) <sub>2</sub>	204
2	<b>13</b>	Ar <sub>2</sub> N-	-(CN)C=C(CN) <sub>2</sub>	344
3	<b>17</b>	Ar <sub>2</sub> N-Ar'(OMe)-	-(CN)C=C(CN) <sub>2</sub>	325
4	<b>23</b>	(BuO-Ar) <sub>2</sub> N-	-(CN)C=C(CN) <sub>2</sub>	351
5	<b>21</b>	Bu <sub>2</sub> N-	-CH=C(CN) <sub>2</sub>	321
6	<b>15</b>	(Bu-Ar) <sub>2</sub> N-	-CH=C(CN) <sub>2</sub>	383
7	<b>18</b>	Ar <sub>2</sub> N-Ar'(OMe)-	-CH=C(CN) <sub>2</sub>	375
8	<b>22</b>	Bu <sub>2</sub> N-	-CH=isoxy	233
9	<b>16</b>	(Bu-Ar) <sub>2</sub> N-	-CH=isoxy	242
10	<b>19</b>	Ar <sub>2</sub> N-Ar'(OMe)-	-CH=isoxy	232

#### Photochemical Stability:

The electro-optic devices are exposed to high intensity radiation during its operation. Therefore, for the longevity of these devices, it is necessary that the constituents of the device are photochemically stable. We hypothesized that the decomposition of these NLO dyes could involve the formation of a radical cation on the amino donor through photochemical oxidation and subsequent  $\alpha$ -hydrogen abstraction.<sup>12</sup> We therefore further hypothesized that replacing the alkyl groups with aryl group in the donor part of the chromophore should increase the oxidation potential and also obviate the decomposition mechanism involving the hydrogen atom  $\alpha$ - to the nitrogen. To test such a hypothesis, the photochemical stabilities of the NLO chromophores based on *N,N*-dialkylamino- donor and *N,N*-diarylmino- donor groups are compared. To monitor the decomposition percentage over time, an approximately  $10^{-5}$  M solution of the chromophores in toluene was irradiated for 1 hour at 350 nm and the effect on the UV-visible absorbance was measured. The results are enlisted in Table IV. It is clear that the behaviour of the chromophores depend both on the nature of the donor and the acceptor. It is gratifying to note that the compounds with the diarylmino donors decompose much slower than the corresponding dialkylamino donor based chromophores. However, it is noted that precluding hydrogens  $\alpha$ - to the nitrogen did not completely obviate the degradation process of the diarylmino based chromophores. This result is taken to suggest that additional decomposition pathways operate in the photochemical degradation of these chromophores.

**Table IV:** Photochemical Decomposition Percentage of the NLO Chromophore Solutions in Toluene after 1 hour of irradiation at 350 nm.

Entry	Compound	$R_2N-$	Acceptor	Decomposed (%)
1	<b>20</b>	$Bu_2N-$	$-(CN)C=C(CN)_2$	7.1
2	<b>13</b>	$Ar_2N-$	$-(CN)C=C(CN)_2$	0.9
3	<b>17</b>	$Ar_2N-Ar'(OMe)-$	$-(CN)C=C(CN)_2$	2.4
4	<b>23</b>	$(BuO-Ar)_2N-$	$-(CN)C=C(CN)_2$	2.5
5	<b>21</b>	$Bu_2N-$	$-CH=C(CN)_2$	-(a)

6	<b>15</b>	(Bu-Ar) <sub>2</sub> N-	-CH=C(CN) <sub>2</sub>	-(a)
7	<b>22</b>	Bu <sub>2</sub> N-	-CH=isoX	7.0
8	<b>16</b>	(Bu-Ar) <sub>2</sub> N-	-CH=isoX	3.5

(a) The UV-visible absorbance of the chromophores **15** and **21** oscillated up and down within about 15% of its original value.<sup>13</sup>

### Concluding Remarks

The diarylamino chromophores that were reported here are expected to have similar optical nonlinearities as their dialkylamino counterparts. We have demonstrated, in addition, that this modification results in enhanced photochemical stability and thermal stability of these chromophores. These factors will be important in device fabrication and device longevity. We have also demonstrated that nonlinearities can be significantly enhanced by introducing relatively weakly electron donating moieties in the conjugated bridge. We believe that this study will prove extremely useful in future design of chromophores for electro-optic devices.

## **5. PERSONNEL**

Seth Marder	P. I.
Joseph Perry	P. I.
Peter Bedworth	(Post-Doc)
Chin-Ti Chen	(Post-Doc)
Zhongying Hu	(Post-Doc)
Fabienn Meyers	(Post-Doc)
Harald Roeckel	(Post-Doc)
Stephen Barlow	(Post-Doc)
Matt Lipson	(Post-Doc)
Timo Mangel	(Post-Doc)
Tim Parker	(Post-Doc)
S. Thayumanavan	(Post-Doc)
Qing Tim Zhang	(Post-Doc)
Karen Kustedjo	(Undergraduate student)
Galina Levin	(Technician)
James Quallen	(Undergraduate student)

In addition, several people who are not directly receiving funding from this grant but who are performing work in a collaborative manner include:

Marguerite Barzoukas  
Mireille Blanchard-Desce  
Younming Cai  
Alain Fort  
Alex Jen

## 6. PUBLICATIONS

1. M. Stähelin, M. Alhlein, B. Zysset, S. R. Marder, M. Barzoukas, A. Fort  
“Nonlinear Optical Properties of Novel Push-Pull Polyenes for Electro-optics.” *J. Opt. Soc. Am. B.*, **13**, 2401 (1996).
2. V. Alain, M. Blanchard-Desce, C.-T. Chen, S. R. Marder, A. Fort, M. Barzoukas  
“Large Optical Nonlinearities with Conjugated Ferrocene and Ruthenocene Derivatives.” *Synthetic Metals*, **81**, 133 (1996).
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“Chromophores with Strong Heterocyclic Acceptors: A Poled Polymer with Large Electro-Optic Coefficient.” *Science*, **271**, 335 (1996).
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“Organic Optical Limiter with a Strong Nonlinear Absorptive Response”. *Science*, **273**, 1533 (1996).
5. A. K.-Y. Jen, Y. Cai, P. V. Bedworth, S. R. Marder  
“Synthesis and Characterization of Highly Efficient and Thermally Stable Diphenylamino-Substituted Thiophene Stilbene Chromophores for Nonlinear Optical Applications.” *Adv. Mater.*, **9**, 312 (1997).
6. F. Meyers, C.-T. Chen, S. R. Marder, J.-L. Brédas  
“Electronic Structure and Linear and Nonlinear Optical Properties of Symmetrical and Unsymmetrical Squaraine Dyes.” *Chem. Eur. J.*, **4**, 530 (1997).
7. M. Blanchard-Desce, V. Alain, P. V. Bedworth, S. R. Marder, A. Fort, C. Runser, M. Barzoukas  
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8. G. U. Bublitz, R. Ortiz, C. Runser, A. Fort, M. Barzoukas, S. R. Marder, S. G. Boxer  
“Stark Spectroscopy of Donor-Acceptor Polyenes: Correlation with Non-linear Optical Measurements.” *J. Am. Chem. Soc.*, **119**, 2311 (1997).
9. G. U. Bublitz, S. G. Boxer, S. R. Marder, R. Ortiz  
“Measurements of the Electronic Structure of Donor/Acceptor Substituted Polyenes and Their Relation to the First Molecular Hyperpolarizability  $\beta$ .” *J. Am. Chem. Soc.*, **119**, 3365 (1997).
10. S. R. Marder, W. E. Torruellas, M. Blanchard-Desce, V. Ricci, G. I. Stegeman, S. Gilmour, J.-L. Brédas, M. Barzoukas, A. Fort, G. Bublitz, . G. Boxer  
“Large Third-Order Molecular Nonlinearities in Polarized Carotenoids.” *Science*, **276**, 1233 (1997).
11. B. Kippelen, F. Meyers, N. Peyghambarian, S. R. Marder  
“Chromophore Design for Photorefractive Applications.” *J. Am. Chem. Soc.*, **119**, 4559 (1997).
12. P. V. Bedworth, J. W. Perry, S. R. Marder  
“Synthesis of Symmetrically Substituted Octa (iso-pentyloxy) anthralocyanine.” *J. Chem. Soc. Chem. Commun.*, 1353 (1997).
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“Synthesis of Unsymmetrical Triarylaminies for Photonic Applications via One-Pot Palladium-Catalyzed Aminations.” *Chem. Mat.*, **9**, 3231 (1997).
14. S. R. Marder, B. Kippelen, A. K.-Y. Jen, N. Peyghambarian  
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15. B. Kippelen, B. L. Volodin, D. D. Steele, E. Hendrickx, D. Sandalphon, Y. Edami, J. L. Maldonado, J. F. Wang, A. Golemme, H. Röckel, S. R. Marder, J. B. Javidi, N. Peyghambarian  
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“Photorefractive Polymers with Improved Efficiency.” *Proc. CLEO*, **11**, 335 (1997).
17. D. D. Steele, B. L. Volodin, O. Savina, B. Kippelen, N. Peyghambarian, H. Röckel, S. R. Marder  
“Transillumination Imaging Through Scattering Media by Use of Photorefractive Polymers.” *Optics Lett.*, **23**, 153 (1998).
18. B. Kippelen, S. R. Marder, E. Hendrickx, J. L. Maldonado, G. Guillemet, B. L. Volodin, D. D. Steele, Y. Enami, D. Sandalphon, Y. J. Yao, J. F. Wang, H. Röckel, L. Erskine, N. Peyghambarian  
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19. M. Albota, D. Beljonne, J.-L. Brédas, J. Ehrlich, J.-Y. Fu, A. Heikal, S. Hess, T. Kogej, M. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. Webb, X.-L. Wu, C. Xu  
“Design of Organic Molecules with Large Two-Photon Absorption Cross Sections.” *Science*, **281**, 1653 (1998)

## 7. INTERACTIONS/TRANSITIONS

### 7.1 Participation at meetings, conferences, seminars

1. S. R. Marder "*Thin Films for Integrated Optics Applications.*" Held at the Materials Research Society in San Francisco, April 1995. Coorganized with David M. Walba and Bruce W. Wessels.
2. S. R. Marder "*Polymeric and Organic Materials: Solid State Properties and Smart Materials.*" Held at the American Chemical Society National Meeting in Anaheim CA., April 1995. Member of the technical committee, Charles Lee, Robert Singler, Alex K.-Y. Jen, and John Reynolds, organizers.
3. S. R. Marder "*Design of Chromophores for Second-Order Nonlinear Optical Applications*" Presented at American Chemical Society National Meeting, Anaheim, CA, April, 2-7 1995.
4. S. R. Marder (presented by Meyers, F)." *Rational Design of Nonlinear Optical Materials*" Pesented at The Royal Society of Chemistry's Second International Meeting on Materials Chemistry, Kent, England, July, 18-21, 1995. (Plenary Lecture).
5. S. R. Marder (presented by Rafael Ortiz) "*Design of Highly Nonlinear Chromophores for Electro-optic Applications*" Presented at the International Conference on Advanced Materials, Sponsored by the International Research Society, Cancun, Mexico, August 27-30, 1995.
6. S. R. Marder "*Design of Chromophores for Electro-optic Applications*" Presented at Optical Society of America/American Chemical Society Joint Topical Meeting: Organic Thin Films for Photonic Applications, Portland, OR, September 11-14, 1995.
7. S. R. Marder "*Materials for Electro-optic Applications*" Presented at Materials Research Society National Meeting, Boston, MA, November 27-December 1, 1995.
8. S. R. Marder "*Organometallic Chromophores for Nonlinear Optical Applications.*" Presented at The American Chemical Society National Meeting, New Orleans, LA, March 24-28, 1996.

9. S. R. Marder "*Recent Advances in the Design and Application of Organic Molecules with Conjugated Second- and Third-Order Optical Nonlinearities.*" Presented at the Belgium Chemical Society International Conference on Conjugated Polymers, Mons, Belgium, October 10-11, 1996.
10. S. R. Marder "*Recent Advances in the Design and Use of the Real and Imaginary Third-Order Optical Nonlinearities of Organic Dyes*" Presented at The Third International Conference on Organic Nonlinear Optics, Marco Island, FL, December 15-20, 1996.
11. S. R. Marder "*Nonlinear Absorbing Chromophores.*" Presented at the American Physical Society National Meeting, Kansas City, MO, March, 16-21, 1997.
12. S. R. Marder "*Optimizing the Real and Imaginary Third-Order Optical Nonlinearities of Organic Molecules.*" OPTIMAS Workshop on Nonlinear-Optical Properties of Polymers and Related Topics, Bayreuth, Germany, June 30- July 1, 1997.
13. S. R. Marder "*Chromophores for Multiphoton Processes.*" Presented at the Jute Conference of Unconventional Photoactive Systems, Nara, Japan, August, 1997.
14. S. R. Marder "*Structure/Property Relationships for Organic Nonlinear Optical Materials*," Presented at Nonlinear Optical Materials Mini Symposium,Taipei, Taiwan, March 12, 1998
15. M. Rumi, A. A. Heikal, J. Fu, S. Barlow, M. D. Levin, L. Erskine, D. McCord-Maughon, H. Röckel, G. Subramaniam, S. Thayumanavan, J. W. Perry, S. R. Marder, T. Kogej, D. Beljonne J.-L. Brédas, M. Albota, C. Xu, W. W. Webb "*The Design of Molecules with Large Two-Photon Absorptivities.*" Presented at CLEO/IQEC National Meeting, San Francisco, May 1998
16. S. R. Marder "*Design, Synthesis and Applications of Organic Nonlinear Optical Materials.*," Presented at New Frontiers in Functional Organic Nanomaterials, Schloß Ringberg, June 26, 1998

17. S. R. Marder "New Molecules for EO Polymers." Presented at 1998 IEEE/LEOS Summer Topical Meetings, Monterey, CA, July 1998
18. S. R. Marder, S. Barlow, D. Beljone, J.-L. Brédas, B. H. Cumpston, J.-Y. Fu, J. E. Ehrlich, A. A. Heikal, T. Kogej, M. D. Levin, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, S. Thayumanavan, X.-L. Wu "Design, Synthesis, and Applications of Two-Photon Absorbing Organic Molecules.", Presented at the American Chemical Society National Meeting, Boston, MA, August 27, 1998
19. S. R. Marder "Design, Synthesis and Applications of Two-Photon Absorbing Chromophores." Presented at the Francqui Symposium, Brussels, Belgium, October 21-23 1998

## 7.2 Consultative and advisory functions

None.

## 7.3 Transitions

1. Various phthalocyanine and naphthalocyanine compounds synthesis in our groups have been transitioned to Dr. Patrick Hood of Wright Laboratory for further testing in their optical limiting program.
1. a. Various thiophene containing chromophores developed in this program have been transitioned to Dr. Alex Jen Northeastern, George Stegeman at U. Fl CREOL, Susan Ermer, at Lockheed-Martin, and Hillary Lackritz at Gemfire for evaluation.
2. a. Various chromophores developed in this program have been transitioned to Dr Nasser Peyghambarian and Bernard Kippelen of AZ, U of at Tucson, for incorporation in the photorefractive composites.

## 8. NEW DISCOVERIES

1. S. R. Marder, N. Peyghambarian, B. Kippelen, B. Volodin, E. Hendrick "Thermally Stable Molecules with Large Dipole Moment and Polarizabilities and Applications Thereof" U.S. Patent Application, Filed May 13, 1998.

## 9. HONORS/AWARDS

S. R. Marder, Member, Board of Reviewing Editors for *Science*.

S. R. Marder and J. W. Perry. 7/97-6/99 NSF Special Creativity Award Extension

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<sup>1</sup> (a) Nonlinear Optical Properties of Organic Molecules and Crystals; Chemla, D.S.; Zyss, J. Eds.; Academic Press; New York, 1987. (b) Materials for Nonlinear Optics: Chemical Perspectives; Marder, S.R.; Sohn, J.E.; Stucky, G.D. Eds.; *ACS Symposium Series*, **1991**. (c) Optical Nonlinearities in Chemistry; special issue of *Chem. Rev.* **1994**, *94*, issue no. 1. (d) Marder, S.R.; Perry, J.W. *Science*, **1993**, *263*, 1706.

<sup>2</sup> For a recent review, see: Marder, S.R.; Kippelen, B.; Jen, A.K.-Y.; Peyghambarian, N. *Nature*, **1997**, 845.

<sup>3</sup> (a) Marder, S.R.; Beratan, D.N.; Cheng, L.-T. *Science*, **1991**, *252*, 103. (b) Gorman, C.B.; Marder, S.R. *Proc. Natl. Acad. Sci.* **1993**, *90*, 11297. (c) Meyers, F.; Marder, S.R.; Pierce, B.M.; Brédas, J.L. *J. Am. Chem. Soc.* **1994**, *116*, 10703 and references therein.

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<sup>6</sup> (a) Dalton, L.R.; Harper, A.W.; Robinson, B.H. *Proc. Nat. Acad. Sci. USA*, **1997**, *94*, 4842. (b) Harper, A.W.; Sun, S.; Dalton, L.R.; Garner, S.M.; Chen, A.; Kalluri, S.; Steier, W.H.; Robinson, B.H. *J. Opt. Soc. Am. B. Opt. Phys.* **1998**, *15*, 329.

<sup>7</sup> For chromophores with styryl thiophene bridging group, see: (a) refer to Jen, Rao, two papers & Gilmour, Marder paper again here. (b) Rao, V.P.; Jenn, A.K.-Y.; Wong, K.Y.; Drost, K. *Tetrahedron Lett.* **1993**, *34*, 1747. (c) Wong, K.Y.; Jen, A.K.-Y.; Rao, V.P.; Drost, K.J. *Appl. Phys. B* **1995**, *61*, 191.

<sup>8</sup> (a) Driver, M.S.; Hartwig, J.F. *J. Am. Chem. Soc.* **1996**, *118*, 7217. (b) Wolfe, J.P.; Wagaw, S.; Buchwald, S.L. *J. Am. Chem. Soc.* **1996**, *118*, 7215. (c) Hartwig, J.F. *SYNLETT*, **1997**, 329.

<sup>9</sup> Thayumanavan, S.; Barlow, S.; Marder, S.R. *Chem. Mater.* **1997**, *9*, 3231.

<sup>10</sup> Unpublished results from Caltech and Northeastern University.

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<sup>11</sup> At this point, the chromophore also lost its strong charge transfer absorption in the visible region.

<sup>12</sup> Such a possibility has been proposed in metal catalyzed oxidative decomposition of *N,N*-dialkylanilines, see: Baciocchi, E.; Lanzalunga, O.; Lapi, A.; Manduchi, L. *J. Am. Chem. Soc.* **1998**, *120*, 5783 and references cited therein.

<sup>13</sup> The origin of such a fluctuation is not clear. The sample was checked by <sup>1</sup>H NMR after 15 minutes and 60 minutes of irradiation to rule out the possible trans-cis isomerization. The chromophores was purely trans by NMR in both these samples. There were no other identifiable impurities in these samples.